

## A valence force field for nickel porphin and copper porphin

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**Abstract**—Normal coordinate calculations have been carried out for nickel porphin and copper porphin on the basis of a constrained valence force field. Resonance Raman spectra of nickel porphin have been obtained with 488.0 nm excitation. A 25 parameter force field was employed to calculate a total of 103 frequencies. Eighteen force constants were refined to obtain a least squares fit. The planar modes are described in terms of the potential energy distribution. Several modes in each molecule can be classified as predominantly CH bending vibrations,  $C_\alpha$ - $C_m$  stretching vibrations and pyrrole ring stretching vibrations.

### INTRODUCTION

Over the past few years much attention has been devoted to the resonance Raman spectra of heme proteins [1-8 and references therein] and to the structurally related porphyrins and porphins [9-13 and references therein]. Empirical correlations have been established between the valence and spin state of the iron in heme proteins and observed resonance Raman lines [6, 14]. The observed lines have been classified by their polarization characteristics [4, 6, 9-13] and some qualitative group frequency assignments have been proposed [6, 9-13]. OGOSHI *et al.* have published a partial normal coordinate analysis of some metal porphins, based on a Urey-Bradley type force field [15]. Only the 18 i.r. active  $E_u$  modes were included, and only a few force constants were refined. The average frequency error was around  $27\text{ cm}^{-1}$ . STEIN *et al.* have calculated the frequencies of 12 Raman active fundamentals in the frequency range  $1000\text{--}1700\text{ cm}^{-1}$  of octamethyl-porphin and compared the results with the observed frequencies of cytochrome C [8]. A modified Urey-Bradley force field was employed; the methyl groups were treated as point masses. ABE, KITAGAWA and KYOGOKU have calculated the Raman active modes of Ni-octamethyl porphin and Ni-octamethyl porphin- $d_4$  in the  $1000\text{--}1650\text{ cm}^{-1}$  range [27].

The present communication reports a normal coordinate analysis of copper porphin and nickel porphin involving all planar modes of both compounds. A 25 parameter valence type force field is employed. Some stretching force constants are evaluated with the help of bond length correlations [16, 17]. Eighteen force constants are refined to obtain a least squares fit for a total of 103 observed frequencies.

### DATA AND INSTRUMENTATION

Free porphin was purchased from the Sigma Chemical Company\* and used without further purification. Ni-porphin was prepared by the method described by ADLER *et al.* [18]. The absorption spectra of Ni-porphin showed characteristic bands at 398, 510 and 543 nm in  $\text{CS}_2$  solution, and no trace of the free porphin. Resonance Raman spectra were obtained with a Spex Ramalog system equipped with an RCA C-31034 photomultiplier, photon counting and a Carson model 101 argon ion laser. A flow cell was used to prevent sample decomposition in the laser beam. The sample was kept at  $2\text{--}3^\circ\text{C}$ ; the concentration was  $\sim 10^{-4}\text{ M}$ . Resonance Raman spectra were obtained in  $\text{CS}_2$  and tetrachloroethylene solution with 4880 Å and 5145 Å excitation.

Data obtained with 5145 Å excitation are in excellent agreement with spectra published very recently by VERMA *et al.* [9]. The spectra observed with 4880 Å excitation exhibit considerably more intense polarized lines ( $A_{1g}$ ) in the range  $900\text{--}1750\text{ cm}^{-1}$  than the spectra observed with 5145 Å excitation. Five polarized lines, including a strong line assigned to a fundamen-

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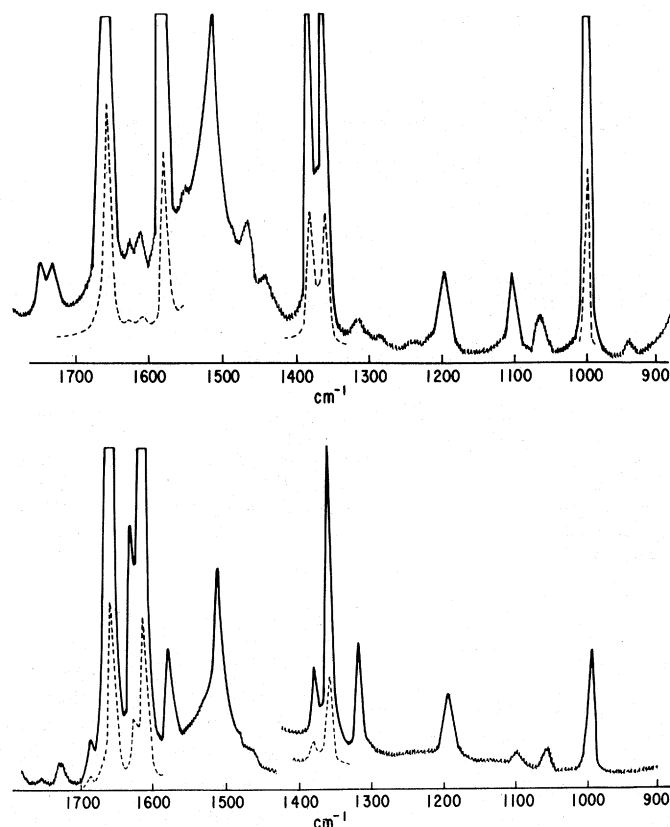


Fig. 1. Resonance Raman spectrum of nickel porphin, 900–1800  $\text{cm}^{-1}$ . 448.0 nm excitation. Concentration  $\text{ca. } 10^{-4}$  M. Upper diagram, electric vector of scattered radiation parallel to electric vector of incident laser beam. Lower diagram, electric vector of scattered radiation perpendicular to electric vector of laser beam. Dotted lines,  $\sim 1/4$  intensity of solid lines, same polarization.

tal mode ( $1575 \text{ cm}^{-1}$ , see below) can be observed only with  $4880 \text{ \AA}$  excitation. These spectra are shown in Fig. 1; the observed polarized lines are listed in Table 1. Two low frequency depolarized lines (240 and  $182 \text{ cm}^{-1}$ ), on the other hand, are evidently observed only with  $5440 \text{ \AA}$  excitation [9]. Literature data were used for the resonance Raman lines of Cu-porphin [10] and the i.r. absorption bands of Cu- and Ni-porphin [15].

#### COMPUTATIONS

##### Numerical methods and structural considerations

Numerical calculations, based on the GF-matrix formulation [19], were carried out by applying previously employed procedures and computer programs [16]. The problem was set up in terms of internal valence coordinates.  $D_{4h}$  symmetry was assumed for Cu-porphin and Ni-porphin [15]. Only the in-plane modes were calculated. There are no resonance Raman lines for out-of-plane vibrations [4, 10]

because of the planar symmetry of the electronic transitions. The planar modes are classified as:

$$9 A_{1g} + 8 A_{2g} + 9 B_{1g} + 9 B_{2g} + 18 E_u$$

All *gerade* modes are resonance Raman-active. The  $A_{1g}$  modes are polarized, the  $A_{2g}$  modes inversely polarized, the  $B_{1g}$  and  $B_{2g}$  modes are depolarized [4]. The 18  $E_u$  modes are i.r.-active only. Six out-of-plane  $A_{2u}$  modes are also i.r.-active and complicate the assignments of the planar  $E_u$  modes [15].

##### G-matrices and symmetry coordinates

G-matrices were calculated on the basis of the molecular parameters of bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron (II) [8, 20], assuming  $D_{4h}$  symmetry for the porphinato core [20] and a bond length of  $1.09 \text{ \AA}$  for the C—H bonds [15].

Symmetry coordinates were constructed from equivalent internal displacement coordinates in a manner analogous to the  $E_u$  symmetry coordinates reported by OGOSHI *et al.* [15]. Such coordinates are

Table 1.  $A_{1g}$  vibrations of metal porphins ( $\text{cm}^{-1}$ )

Cu-porphin		Ni-porphin		$\nu$	Potential energy distribution $\ddagger$
Obs.*	Calc.	Obs. $\dagger$	Calc.		
3081 <i>w</i>	3095	3110 <i>w</i>	3095	1	1 98
3010 <i>vw</i>	3024		3024	2	2 99
		1745 <i>w</i>			
	1709		1709	3	3 38, 5 19, 17 10
1562 <i>s</i>	1581	1575 <i>s</i>	1584	4	4 37, 6 21, 10 34
		1545 <i>w</i>			
		1461 <i>w</i>			
1425 <i>w</i>		1440 <i>w</i>			
1370 <i>w</i>	1378	1379 <i>s</i>	1379	5	3 51, 5 19, 6 32
1336 <i>sh</i>					
1098 <i>vw</i>	1101	1103 <i>w</i>	1102	6	13 92
1065 <i>sh</i>		1067 <i>vw</i>			
998 <i>s</i>	1002	996 <i>s</i>	1015	7	4 55, 5 18, 10 9
732 <i>m</i>	712	732 <i>m</i>	711	8	4 16, 5 19, 15 10, 16 25
368 <i>s</i>	352	371 <i>m</i>	367	9	6 27, 8 19, 16 17 (Cu) 6 27, 7 23, 16 15 (Ni)

\* Ref. 10, resonance Raman.

 $\dagger$  4880 Å excitation, resonance Raman. $\ddagger$  See Fig. 2. First number designates valence force constant, second number % PED.

somewhat artificial and serve for computational purposes only. They contain a considerable number of redundancies [15] and cannot be related to normal vibrations in a simple manner (i.e., no pure bending modes are physically feasible, except for the outer C—H bonds).

#### The force field

The  $F$ -matrices were constructed in terms of internal valence coordinates. For molecules of high complexity a carefully chosen valence force field frequently yields better results than the often-used Urey-Bradley approximation [16, 21–23]. It also has the

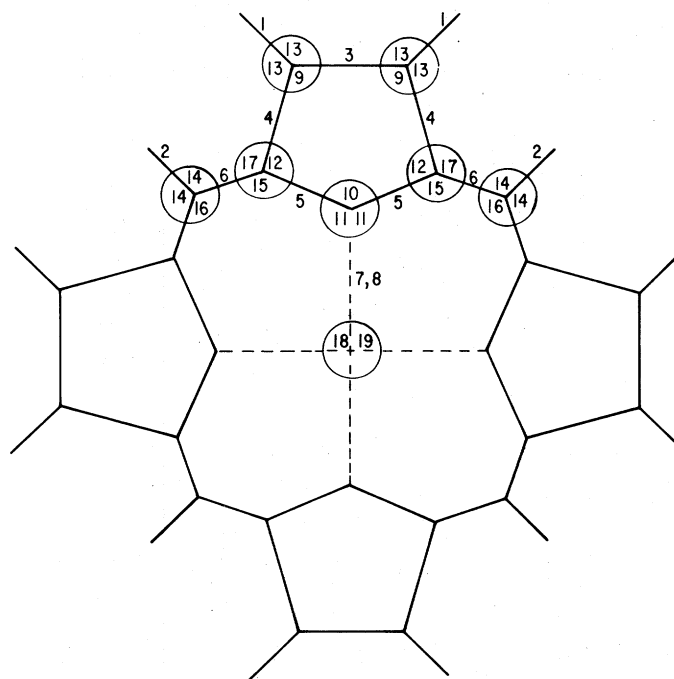


Fig. 2. Schematic structure of metal porphins and numbering of diagonal force constants. Force constants 7 and 18 are for nickel porphin only; 8 and 19 for copper porphin only.

Table 2.  $A_{2g}$  vibrations of metal porphins ( $\text{cm}^{-1}$ )

Cu-porphin		Ni-porphin		$\nu$	Potential energy distribution $\ddagger$
Obs.*	Calc.	Obs. $\dagger$	Calc.		
	3096		3096	10	1 98
1690 <i>m</i>		1685 <i>m</i>			
		1621 <i>m</i>			
1587 <i>s</i>	1598	1606 <i>vs</i>	1598	11	4 26, 6 73
	1486	1485 <i>vw</i>	1486	12	4 32, 5 21, 9 37
		1372 <i>w</i>			
1322 <i>s</i>	1353	1320 <i>vs</i>	1352	13	5 27, 6 15, 13 24, 14 29
		1174 <i>w</i>			
1143 <i>vw</i>	1151	1139 <i>m</i>	1151	14	13 52, 14 38
	1064		1064	15	5 42, 13 15, 14 34
		949 <i>vw</i>			
802 <i>w</i> $\S$	786	805 $\S$	786	16	4 33, 5 20, 9 35
498 <i>sh</i>	479		479	17	15 32, 17 54

\* Ref. 10, resonance Raman.

 $\dagger$  5145 Å excitation, resonance Raman. $\ddagger$  As in Table 1. $\S$  In  $\text{C}_2\text{Cl}_4$  solution.

advantage that bond length-force constant correlations can be used in a straightforward manner [16, 17, 21, 24].

The diagonal terms of the  $F$ -matrix were numbered as shown in Fig. 2. Interaction terms were chosen by a scheme which has been previously used with

fair success on some large heterocyclic molecules [17, 21]: (a) In general, only stretch-stretch interactions with one common atom and stretch-bend interactions with two common atoms are included. (These are the valence force field interactions resulting from a Urey-Bradley force field with *gem* interactions.) (b)

Table 3.  $b_g$  vibrations of metal porphins ( $\text{cm}^{-1}$ )

Cu-porphin		Ni-porphin		$\nu$	Potential energy distribution $\ddagger$
Obs.*	Calc.	Obs. $\dagger$	Calc.		
$B_{1g}$		$B_{1g}$			
	3095		3095	18	1 99
	1678		1681	19	3 34, 5 16, 10 12
1631 <i>s</i>	1651	1651 <i>m</i>	1652	20	3 19, 4 16, 6 61
1380 <i>w</i>	1377	1356 <i>s</i>	1380	21	3 37, 5 36, 6 32
1180 <i>m</i>	1189	1186 <i>m</i>	1189	22	14 92
	1101	1123 <i>vw</i>	1102	23	13 91
1004	976	1003 <i>s</i>	985	24	4 80
	777		779	25	5 15, 10 23, 17 18
206	217	240 <i>w</i>	238	26	7 49, 15 18, 17 15 (Ni)
					8 42, 15 20, 17 20 (Cu)
$B_{2g}$		$B_{2g}$			
	3096		3096	27	1 99
	3024		3024	28	2 99
1547 <i>sh</i>	1553	1538 <i>vw</i>	1554	29	3 15, 4 28, 5 39
1498 <i>s</i>	1535	1505 <i>m</i>	1535	30	4 46, 9 31
1210 <i>vw</i>	1204	1195 <i>m</i>	1204	31	13 73
1059 <i>m</i>	1055	1060 <i>s</i>	1060	32	5 66, 6 14
	932		932	33	9 37, 16 25
426 <i>vw</i>	433		433	34	4 18, 6 26, 17 27
	149	182 <i>w</i>	166	35	11 10, 18 37, 16 26 (Ni)
					11 12, 16 26, 19 23 (Cu)

\* Ref. 10, resonance Raman.

 $\dagger$  5145 Å excitation, resonance Raman. $\ddagger$  As in Table 1.

Table 4.  $E_u$  vibrations of metal porphins ( $\text{cm}^{-1}$ )

Cu-porphin		Ni-porphin		$\nu$	Potential energy distribution†
Obs.*	Calc.	Obs.*	Calc.		
3120 w	3096		3096	36	1 98
3120 w	3096		3095	37	1 98
3025 w	3024	3030 w	3024	38	2 99
1715 m	1694	1710 w	1696	39	3 39, 5 19
1655 w	1636	1655 w	1637	40	6 63, 10 18
1567 w	1555	1547 m	1556	41	4 41, 6 29
1534 m	1509		1509	42	4 21, 5 28, 9 30
1450 w		1463 w			
1387 s	1395	1398 s	1397	43	3 37, 5 25, 6 31
1355 w		1357 w			
1310 s	1276	1320 s	1276	44	5 14, 6 17, 13 22, 14 34
1151 s	1159	1151 s	1159	45	13 49, 14 40
	1101	1068	1102	46	13 90
1057 s	1060	1062 s	1062	47	5 51, 14 22
998 s	996	994 s	1008	48	4 57, 5 13
900 w		894 m			
861 s	858	856 s	858	49	4 24, 9 33, 16 16
848 s		846 s			
		806 w			
774 s		769 s			
745 m	752	744 s	753	50	5 20, 10 13, 17 14
702 s					
698 s		700 s			
392 m	393	420 s	413	51	6 18, 7 32, 17 10
346 s	359	366 m	365	52	15 26, 17 40
		356 s			
246 w		290 m			
234 m	233	282 m	278	53	7 41, 18 14 (Ni) 8 62 (Cu)
223 w		243 m			

\* I.r. absorption bands, Ref. 15.

Observed bands  $1750\text{--}3000\text{ cm}^{-1}$  are not listed.

† As in Table 1.

Stretch-stretch interactions between non-adjacent bonds within the pyrrole rings were added. (c) All interactions involving CH stretching modes were neglected. In practice, it was also necessary to set all interaction terms involving the metal-nitrogen bonds equal to zero, because they could not be determined from the available data.

The values of CN and CC stretching force constants were evaluated from bond length data [20] as previously described [17], and these force constants were not refined. Initial values for the bending and interaction force constants (except the ones involving the MN bonds) were transferred from pyrrole [25] and pyrimidine bases [21]. The values for MN stretching constants, NMN bending constants, and CNM bending constants were taken from the work of OGOSHI *et al* [15]. (The repulsive constants involving the  $\text{MN}_4$  grouping are very small [15], suggesting that the valence force field interaction terms are also small.)

#### Refinement of force constants

Initial refinements were carried out with the CC and CN stretching force constants fixed (as discussed) and all others subjected to a least squares refinement. The results indicated that additional constraints must be used to obtain computationally meaningful results, i.e., to keep the computational uncertainties of the evaluated force constants within reasonable limits. Simplifications which have led to reasonable results in previous studies with large heterocyclic molecules [17, 21] were employed: (a) All nonadjacent stretch-stretch interactions within the pyrrole rings were assumed to be equal. (b) All stretch-bend interactions involving CC and CN bonds were set equal. (c) All stretch-bend interactions involving CC and CH bonds were set equal. (d) The NMN bending constants were not refined and the interactions involving the NMN grouping were set equal to zero. The calculated force constant values are within the expected

Table 5. Valence force constants of metal porphins

Designation*	Value	Dispersion	Designation*	Value	Dispersion
Diagonal			F (14)	0.446	0.010
F (1)	5.170	0.042	F (15)	0.604	0.106
F (2)	4.956	0.026	F (16)	1.301	0.107
F (3)	8.520	—	F (17)	1.301	0.107
F (4)	5.950	—	F (18)†	0.307	—
F (5)	5.980	—	F (19)‡	0.149	—
F (6)	7.040	—	Interaction		
F (7)†	1.397	0.178	f(CC, CC)	0.496	0.076
F (8)‡	0.939	0.128	f(CC, CN)	0.964	0.079
F (9)	2.267	0.119	f(CN, NC)	0.414	0.124
F (10)	3.582	0.233	f(Str.-str.)	0.786	0.045
F (11)	0.050	—	nonadjacent§		
F (12)	0.604	0.105	f(Str.-bend, skeletal)	0.227	0.029
F (13)	0.427	0.007	f(str.-bend, $\delta$ CH, v skel.)	0.353	0.050

\* See Fig. 2. Str.: mdyn/Å bend.: Å/rad<sup>2</sup>; str. bend: mdyn/rad.

† Ni-porphin only.

‡ Cu-porphin only.

§ Within pyrrole rings.

|| See text for further explanation.

range, except for F(9) and F(10), which are higher than the relatively high values for similar force constants in pyrrole [25].

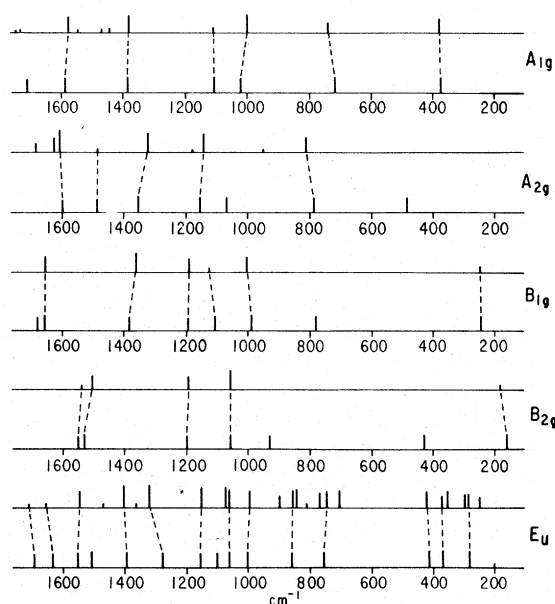


Fig. 3. Schematic correlation of observed and calculated frequencies for Ni-porphin. Upper lines, observed frequencies; lower lines, calculated frequencies.

## RESULTS AND DISCUSSION

Tables 1 to 4 give the assigned and calculated frequencies of the fundamental modes, and the predominant contributions to the potential energy distribution [26] in terms of diagonal valence force constants (cf. Fig. 2). Table 5 lists the final values of the force constants and the computational uncertainties of the refined terms. Figure 3 presents an overall view of the assigned and calculated frequencies below 1700 cm<sup>-1</sup>. The overall average frequency error is ca. 12 cm<sup>-1</sup>, or 1.2%.

It is obvious that in molecules of this size and structure, very few modes can be regarded as separable bond stretching or bending vibrations, with the exception of CH stretching and, possibly, some CH bending modes. The assignment of CH stretching modes is based primarily on infrared data [15] and is somewhat uncertain because the  $A_{1g}$ ,  $A_{2g}$ ,  $B_{1g}$ , and  $B_{2g}$  CH stretches are not observed in the resonance Raman spectra, although we observe numerous overtone and combination bands. A total of 9 modes can be assigned to various CH bending vibrations on the basis of the potential energy distribution, if a CH bending contribution of more than 50% is taken as a criterion. By the same criterion three modes are predominantly  $C_\alpha$ - $C_m$  stretching vibrations involving primarily force constant 6 (see Fig. 2). In addition, a number of modes can be called pyrrole ring stretching vibrations, involving primarily force constants 3,

4 and 5 (Fig. 2). No separable skeletal bending modes are expected or observed.

In the  $A_{1g}$  block,  $\nu_3$ ,  $\nu_5$  and  $\nu_7$  are predominantly pyrrole ring stretching vibrations. They give rise to strong resonance Raman lines at 1379 and 996  $\text{cm}^{-1}$  for Ni-porphin (the highest one is not observed).  $\nu_6$  is an almost pure bending mode of pyrrole hydrogens.

The  $A_{2g}$  modes can be described in a similar manner.  $\nu_{11}$  is essentially a  $C_\alpha-C_m$  stretching mode (force constant 6, 73%). It gives rise to a very strong line for Ni-porphin at 1606  $\text{cm}^{-1}$ .  $\nu_{14}$  is a CH bending mode involving all hydrogen atoms. Three modes,  $\nu_{12}$ ,  $\nu_{13}$ , and  $\nu_{16}$  have moderate pyrrole ring stretching contributions ( $\sim 53\%$  each).

The  $B_{1g}$  and  $B_{2g}$  modes are both depolarized and can be distinguished only by the results of the calculations. Some observed lines are very close to one another and the assignment in these cases must be regarded as tentative. Of the calculated  $B_{1g}$  vibrations  $\nu_{20}$  is again predominantly a  $C_\alpha-C_m$  stretching mode, involving force constant 6.  $\nu_{21}$  and  $\nu_{24}$  are essentially pyrrole ring stretching modes, involving force constants 3 and 5, and 4, respectively.  $\nu_{22}$  is an almost pure pending mode of the *meso* hydrogens,  $\nu_{23}$  an almost pure bending vibration of the pyrrole hydrogens. The  $B_{2g}$  modes exhibit one pyrrole hydrogen bending vibration,  $\nu_{31}$ , and two pyrrole ring stretching vibrations,  $\nu_{29}$  and  $\nu_{32}$ . The latter is predominantly a CN stretching mode.

This leaves the infrared active  $E_u$  modes. The assignment here is complicated by the presence of the i.r. active  $A_{2u}$  vibrations. Four calculated modes,  $\nu_{39}$ ,  $\nu_{43}$ ,  $\nu_{47}$  and  $\nu_{48}$  have strong pyrrole ring stretching contributions, the last two being primarily associated with force constants 5 and 4, respectively.  $\nu_{44}$  and  $\nu_{45}$  are hydrogen bending vibrations, both involving all hydrogen atoms to some degree.  $\nu_{46}$  is a pyrrole hydrogen bending mode;  $\nu_{40}$  is primarily a  $C_\alpha-C_m$  stretching mode.

No distinct set of vibrations could be assigned to the central  $\text{MN}_4$  grouping. Most MN stretching and NMN bending vibrations are strongly mixed with other low frequency modes. One relatively pure NM stretch is  $\nu_8$  in the  $E_u$  block of Cu-porphin (62%). The corresponding Ni-porphin vibration has only 41% NM stretching character. In the  $B_{1g}$  block,  $\nu_{26}$

has a partial MN stretching character for both Cu- and Ni-porphin.

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